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(54) Surface processing of a substrate material

(57) A process for the surface processing of substrate material such as a heat sensitive plastics material comprises exposing the surface of the substrate to a high intensity pulsed plasma of low average power. The pulsed plasma preferably has a mark-space ratio greater than 1:1 chosen so that the total energy over a period of time does not damage the heat sensitive plastic material. The plasma may be provided by applying a high frequency oscillating electric field to a gas and in addition particles may be added to the plasma from a target at which a beam of charged particles is directed.

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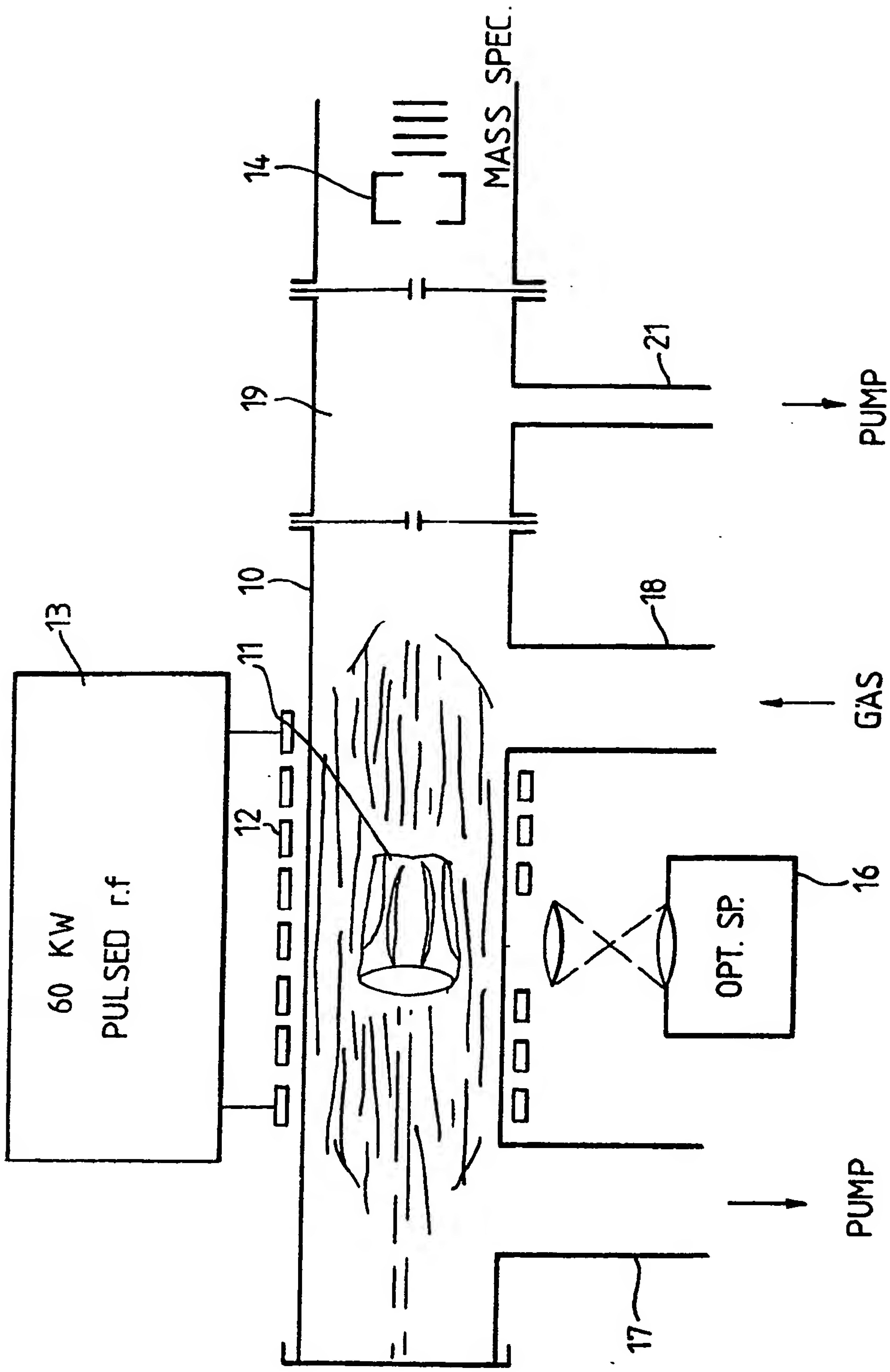

60 KW
PULSED r.f
13
11
12
10
19
14
MASS SPEC.
21
PUMP
18
GAS
16
OPT. SP.
PUMP
17

SPECIFICATION

Surface processing of a substrate material

The present invention relates to the surface processing of a substrate material. Plasma processing and in particular low temperature glow discharge plasma processing is potentially a very useful process for the surface processing of substrate materials. As a source of high energy radiation it can promote both physical and chemical changes at the surface of the substrate and can be used for etching, roughening, polymerisation, cross-linking, adhesion promotion, grafting and coating of the surface. It is possible to include more than one of these processes during a treatment so that one can sequentially carry out surface etching, cross-linking and layer or multilayer deposition of a substrate by simply changing the gas composition. Such a process ensures the maximum possible adherence and compatability between different deposited layers and avoids other problems such as internal optical reflection caused by abrupt interfaces.

However, the deposition of good inorganic coating in normal discharges requires substrate temperatures in excess of 250°C (too high for most plastic substrates for example). The reason for this is probably the relatively low degree of molecular dissociation in the normal discharges. The species arriving at the substrate surface therefore requires additional energy for further decomposition and for structural arrangement of the coating. This has therefore limited the use of plasma in surface processing of many materials and in particular heat sensitive materials such as plastics.

This invention provides according to one aspect a process for surface processing a heat sensitive substrate material comprising exposing the surface of the substrate to a high intensity pulsed plasma of low average power.

By using a plasma of low average power thereby minimising the problems of heating we may use a high intensity plasma on a heat sensitive substrate. One way in which we can achieve this is by using a mark-space ratio of less than unity (i.e. longer space than mark) and we can vary the mark-space ratio of the pulses to suit the substrate, the plasma and desired effect concerned.

In another aspect of the invention there is provided a process for surface processing a substrate material comprising exposing the surface of the substrate to a high intensity pulsed plasma of mark-space ratio less than 1:1.

We may provide pulses of various mark-space ratios for example 1:1 downwards and preferably less than 1:10 and in certain instances the mark-space ratio may be as low as 1:10,000.

In a particular arrangement the pulse length may be 10 μs to 1 ms at a pulse frequency of 10 μs to 1s intervals ("s"=second).

The pulse frequency may be 50 KHz to 30 MHz.

The process may be used for coating, etching, cross-linking, surface heating, grafting, roughening or adhesion promotion.

An electrical potential may be applied to the substrate and in a particularly preferred arrangement this electrical potential may be approximately 1000 volts. The electrical potential may be continuous or pulsed and will normally be negative with respect to the plasma voltage.

Preferred arrangements of the invention will now be described by way of example only and with reference to the accompanying drawing which shows plasma apparatus for carrying out the process of the invention.

The surface processing of a substrate material by a plasma potentially has very many uses. For example, where the present use of a material is based on its surface properties, it allows the use of a cheaper, lighter or otherwise preferred substrate material to be coated with the material whose properties are desired. For example, a plastic substrate material is often preferred for cheapness and lightness whereas the surface properties of glass which is hard and scratch resistant is preferred. The use of a plasma process to coat plastic material with a layer of glass would improve its wear and abrasion resistance, would make it water and dirt repellant, and would allow for the production of a lighter and cheaper item. There are many uses for such material but a particular use which is envisaged is in the side windows of motor vehicles and the reflectors and lamp covers of motor vehicles.

As well as telephones, taps and other domestic parts and plastic packaging of integrated circuits and other electrical components, other uses of plasma surface processing of plastics material include plastic bumpers and other cosmetic parts where the surface properties of the plastic can be changed so as to give an attractive appearance, abrasion and chemical resistance anti-reflection properties and the like.

As has been mentioned above, it has hitherto not been possible to apply plasma technology to plastics material because they are heat sensitive. However plasma processing provides good throwing power, a low pinhole (defect) count, is flexible, not only in the film material to be coated but also in respect of the coating process.

The present invention describes a process for surface processing a substrate material (such as a plastics material) comprising exposing the surface of the substrate to a high intensity pulsed plasma. By pulsing the plasma and suitably selecting the mark-space ratio, high intensity plasma can be used but the overall energy input is sufficiently low not to adversely affect plastic material. It will be understood that although the process will be described with reference to a heat sensitive material such as plastic the principles would also apply to other materials which are less heat sensitive such as steel.

The process is particularly useful in producing articles for use in the automative, sanitary, industrial and optical fields.

In the drawing there is shown a sealed chamber 10 in which is mounted the article 11 whose surface is to be processed. Surrounding the part of the sealed chamber 10 in which the article 11 is mounted is a coil 12 connected to a 60 kw pulsed RF generator 13. A mass spectrometer 14 is arranged to view the gases within the chamber 10 and the article may be viewed by means of an optical system 16. The chamber 10 may be evacuated by means of a pump connected to the outlet 17 and gas may be inserted in the chamber by means of the inlet 18. A sealed chamber 19 is provided between the mass spectrometer 14 and the chamber 10 there being provided suitable windows each side of the chamber 19, and a pump may be connected to an outlet 21 of the chamber 19.

In use, the article 11 is inserted within the chamber and the chamber 10 is then evacuated by means of a pump through the outlet 17. When a predetermined level of vacuum has been reached a desired gas may be inserted through the inlet 18. The RF generator 13 may then be switched on so as to provide a pulsed electrical field through the coils 12. The effect of this is to ionise the gas within the chamber 10 and thereby produce a plasma. The ionised particles bombard the surface of the article 11 to carry out the surface processing desired. The mass spectrometer 14 is used in this arrangement to monitor the types and proportion of ions present in the plasma.

When a first coating process is completed, the gas may, if desired, be evacuated through the outlet 17 and a further gas inserted through the inlet 18 to provide a second processing step. If desired all of the gas may be removed from the chamber 10 before inserting a second gas or alternatively the second gas may be inserted at the same time as the first gas is being removed through the outlet 17. In this way two separate surface processing steps may follow one another if the gases are changed in the second above described manner then there will be no surface discontinuities between the two surface processing steps. In the apparatus thus far described the surface of the article 11, particularly if of plastic, may be processed to provide cross-linking in the plastic surface material, polymerisation, and in some instances incorporation of the material in the gas into the surface layer.

The plasma process so far described is suitable for a number of surface processes but to extend the use of the plasma process to include other atoms of elements for which there are no suitable volatile compounds, which includes many metals, an additional processing step and part of the apparatus is provided. Installed within the chamber 10 is a suitable target material, for example silicon carbide or oxide or nitride or titanium nitride or oxide and means may be provided to fire ions at the target material. Material is sputtered from the target into the already existing plasma and is evenly distributed within the plasma by diffusion. In this way atoms or ions of the target material are produced within the plasma which can thereby be coated onto the article 11. The beam bias directed at the target may be continuous although if preferred may be pulsed, but the plasma will be pulsed as in the preceding example. Such a sputtering process may be carried out by a magnetron and the sputtering process may be carried out throughout the process or may be provided for only part of the process. Furthermore the target material may be changed so as to provide a different coating material.

Normally, the article 11, during the process will be at a bias voltage or about 1000 volts, which is negative with respect to the plasma. The frequency at which the pulsing takes place will again be chosen depending upon the materials involved but may typically be between 50 KHz and 30 MHz and the mark-space ratio may be chosen to be greater than 1:1 and will normally be between 1:10 and 1:10000. The pulse intervals will normally be 100 μs to 1s. For plastic materials the pulse length may be 10 μs to 1 ms at 10 ms to 1s intervals which will restrict the average power density to a few hundred watts per litre.

It is believed that although the plasma is pulsed, reactive species are available during the off periods. The chamber 10 should be maintained at about 0.01 torr and power levels of at least a few kW per litre are required.

The range of materials to which the process may be applied is not limited. However, the process is particularly suited for the treatment of heat sensitive materials, both organic and inorganic. It may also be used, however, for surface treating other materials such as steel or aluminium.

The gas chosen will depend upon the process required. Lower substrate temperatures can be used. Atomic species have the advantage of having much higher chemical energies and structural symmetry. Such discharges have further advantages as sources for ultraviolet radiation which will be beneficial to the production of strong cross-linking of plastic surfaces. The article 11 may be made of a wide range of materials including plastics such as acrylics and carbonates. The processing envisaged includes surface cleaning and activation, graft polymer of matching optical properties, gradually phasing into wear resistant hard materials of high refractive index such as silicon carbide or silicon nitride, a quarter wave ($\lambda/4$) inorganic layer of suitable refractive index of, for example, SiO_2, and a gradual layer of thin optically matched water repellant fluorocarbon.

The use of this process is particularly preferred to arrange a moisture impervious layer for, for example infra red lenses, and may be used to coat particles in a fluidised bed arrangement. A magnetic field may be applied to enhance the degree of ionisation. Additional internal and external heating sources may be applied to creat

the right thermal conditions for the article 11. The coupling as illustrated in the drawing between the article and the power source will generally be inductive.

In certain processes, for example when etching, it may be preferable to place the article 11 outside the active region.

In certain arrangements it may be preferred to pulse the gas supply. In a particular arrangement, the process may be used to provide impermeable coatings for plastics for cables.

As an example of the use of the apparatus, a very thin 0.15 um film of titanium nitride has been coated by means of the plasma process of the invention on an underlayer of 3 um thick titanium on PVC plastic. Such a plastic material shows substantial improvements in wear performance. In a pin-on-disc test, in which the substrate was worn against steel ball bearings, there was an improvement by a factor of 20 and in a reciprocating wear test, using a glass loaded polytetra-fluorethylene stud with sand and fast cutting alumina-interposed showed a sixty fold improvement.

Claims

1. A process for surface processing a heat sensitive substrate material comprising exposing the surface of the substrate to a high intensity pulsed plasma of low average power.

2. The process as claimed in claim 1 in which the pulses are of mark-space ratio of less than 1:1.

3. A process for surface processing a substrate material comprising exposing the surface of the substrate to a high intensity pulsed plasma of mark-space ratio less than 1:1.

4. The process as claimed in claim 2 or 3 in which the pulses are of mark-space ratio of less than 1:10.

5. The process as claimed in claim 2, 3 or 4 in which the pulse length is between 10 μs and 1 ms at intervals between 10 μs and 1s.

6. The process as claimed in any of claims 1 to 4 in which the pulse frequently is between 50 KHz and 30 MHz.

7. The process as claimed in any of claims 1 to 6 which an electric potential is applied to the material.

8. The process as claimed in claim 7 in which the electric potential applied to the material is approximately 1000 volts.

9. The process as claimed in any of claims 1 to 8 in which the plasma is produced by a high frequency oscillating electrical field applied to a gas.

10. The process as claimed in claim 9 in which the gas or gas mixture is varied with time to provide different surface processing of the substrate material.

11. The process as claimed in claim 9 in which a succession of layers is coated onto the substrate material by changing the gas or gas mixture with time.

12. The process as claimed in any of claims 1 to 11 in which material for the plasma is provided by a high intensity beam of particles directed at a target material.

13. The process as claimed in claim 12 in which the high intensity beam of particles is provided by a magnetron.

14. A process as claimed in claim 1 or claim 3 substantially as hereinbefore described.

15. Apparatus for carrying out the process of claim 1 or claim 3 comprising a chamber for containing a plasma, electrical means for producing plasma, and means for pulsing said electrical means to produce a pulsed plasma of mark-space ratio of less than 1:1.

16. Apparatus as claimed in claim 15 further including a magnetron to introduce particles into the plasma.

17. A substrate material having a surface processed by the process of any of claims 1 to 14.

New Claims or Amendments to Claims filed on 26 May 1982
Superseded claims1—17

New or Amended Claims:—

1. A process for surface processing a heat sensitive substrate material comprising exposing the surface of the substrate to a high intensity radio frequency pulsed plasma of low average power, the plasma pulse producing a power density of at least a few KW per litre.

2. The process as claimed in claim 1 in which the pulses are of mark-space ratio less than 1:10.

3. The process as claimed in claim 2 in which the pulse length is between 10 microseconds and 1 ms at intervals between 100 microseconds and 1s.

4. The process as claimed in any of claims 1 to 3 in which the radio frequency is between 50 KHz and 30 MHz.

5. The process as claimed in any preceding claim in which an electric potential is applied to the material.

6. The process as claimed in claim 5 in which the electric potential applied to the material is approximatey 1000 volts.

7. The process as claimed in any preceding claim in which the plasma is produced by a high frequency oscillating electrical field applied to a gas.

8. The process as claimed in claim 7 in which the gas or gas mixture is selected to provide different surface processing of the substrate material.

9. The process as claimed in any preceding claim, wherein the substrate surface is cleaned and activated.

10. The process as claimed in any preceding claim, wherein the substrate surface is subjected to ultra violet light to produce cross-linking at a plastics surface.

11. The process as claimed in any preceding claim, wherein a graft polymer of matching optical properties is deposited.

12. The process as claimed in any preceding

claim, wherein a wear resistant hard material is provided by gradually phasing the gasses.

13. The process as claimed in claim 12, wherein the material has a high refractive index.

14. The process as claimed in claim 12 or 13, wherein the material is silicon carbide or silicon nitride.

15. The process as claimed in any preceding claim, wherein a quarter wavelength inorganic layer is provided.

16. The process as claimed in any preceding claim, wherein a layer of thin optically matched water repellant fluorocarbon is provided.

17. The process as claimed in claim 12 in which the wear resistant layer is a succession of layers coated onto the substrate material by changing the gas or gas mixture with time.

18. A process as claimed in claim 1 substantially as hereinbefore described.

19. Apparatus for carrying out the process of claim 1 comprising a chamber for containing a plasma and supporting a substrate material, electrical means for producing the plasma, and means for producing a high intensity radio frequency pulsed plasma of low average power, the plasma pulse producing a power density in the chamber of at least a few KW per litre.

20. Apparatus substantially as hereinbefore described with reference to the accompanying drawing.

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